



CO₂-induced dissolution of ZnO into ionic liquids and its catalytic application for the hydration of propargylic alcohols

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ABSTRACT

An unexpected CO₂-induced dissolution of ZnO into ionic liquids was discovered. This process exhibited high dissolution speed and the dissociated mixture was applied as an efficient Zn-based catalytic system for the CO₂-promoted hydration of propargylic alcohols under atmospheric pressure with broad substrate scope. Moreover, this system could be recycled and reused for at least 16 times with excellent yields continuously obtained, which is an unprecedented record for this reaction. Significantly, this system could employ waste pigments as the ZnO source and work even under flue gas atmosphere. In the mechanistic investigations, the interaction between ZnO, CO₂ and ionic liquids to give N-heterocyclic carbene/CO₂ adducts proved to be the key factor for this specific dissolution. These adducts were further identified to exhibit better reactivity than the normal CO₂ by experimental data and density functional theory (DFT) calculations, which might be responsible for the excellent performance of the abovementioned catalytic system.

1. Introduction

As one of the most common metal elements on the earth, zinc has been discovered, studied and utilized for centuries. Nowadays, zinc and its compounds serve as the key materials in areas of steels [1], alloys [2, 3], batteries [4–7] *etc.* In view of chemistry, these compounds are generally employed as important reducing agents [8] or building blocks [9]. Particularly, utilization of zinc compounds as catalysts has emerged as a hot topic in synthetic chemistry, especially for the constructions of C–C, C–N or C–O bonds [10–14]. Among these multitudinous Zn catalysts, ZnO is probably the simplest and most common one. However, it is also the special and potential one due to its merits of greenness, abundance, economy and harmlessness, which are in accordance with the requirements of green and sustainable development.

Currently, worldwide annual production of ZnO exceeds more than one and half million tons [15,16], which are mainly applied for the further production of rubbers, ceramics, pigments, *etc.* In spite of the diverse advantages, a wide range of ZnO applications also leads to a

considerable amount of ZnO wastes, which may cause environmental problems for its toxicity when unfavorably enriched in soil and potential inhalation hazards known as zinc fever or zinc ague. Nowadays, more than 80% of available recyclable zinc-containing wastes have been recycled [15]. Among them, reusability of ZnO waste is a research hotspot, which could facilitate the traditional manufacturing industry as well as some advanced areas that employ ZnO for light-emitting diodes, transistors, solar cells, catalysts, *etc.*

Nowadays, ZnO is generally employed as a heterogeneous catalyst in the fields such as CO₂ hydrogenation [17,18], syngas conversion [19, 20], *etc.* However, compared with the versatile zinc salts and the emerging zinc complexes, ZnO is seldom reported as a catalyst for the synthesis of fine chemicals or intricate structures. As its innate heterogeneous property, ZnO generally behaves less catalytic activity than the other zinc compounds in these cases and relatively harsh conditions are inevitably required for its effective activation. Therefore, dissolution of ZnO into homogeneous state may be one of the appropriate ways for its further application in this field.

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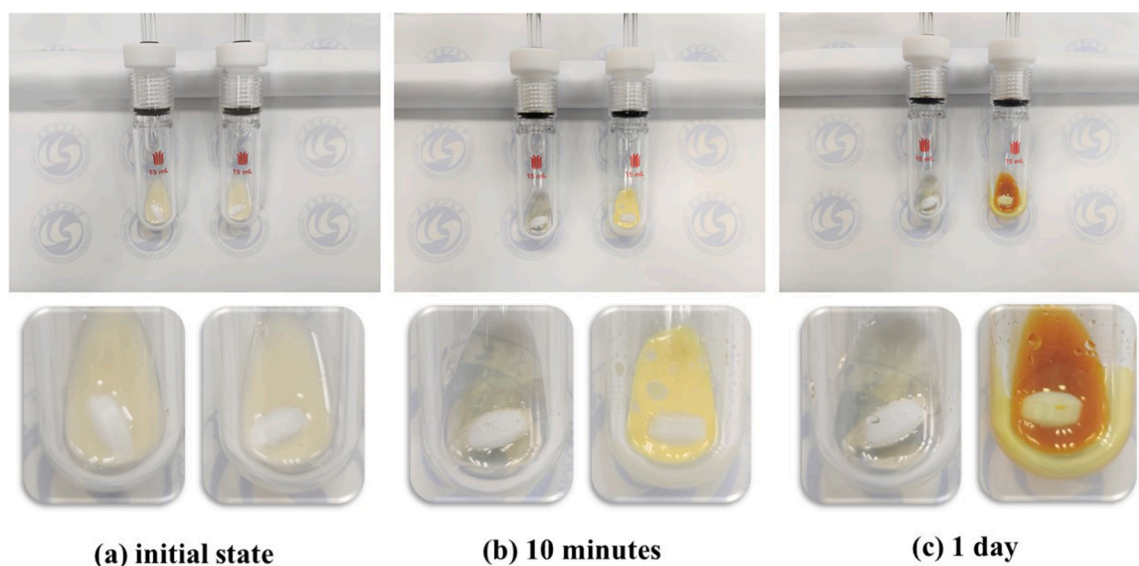


Fig. 1. Different phenomena of ZnO/[C₂C₁im][OAc] with CO₂ (left) and without CO₂ (right). conditions: ZnO: (0.8 mmol), [C₂C₁im][OAc]:(6.28 mmol), 95 °C, 1 bar of CO₂ for left.

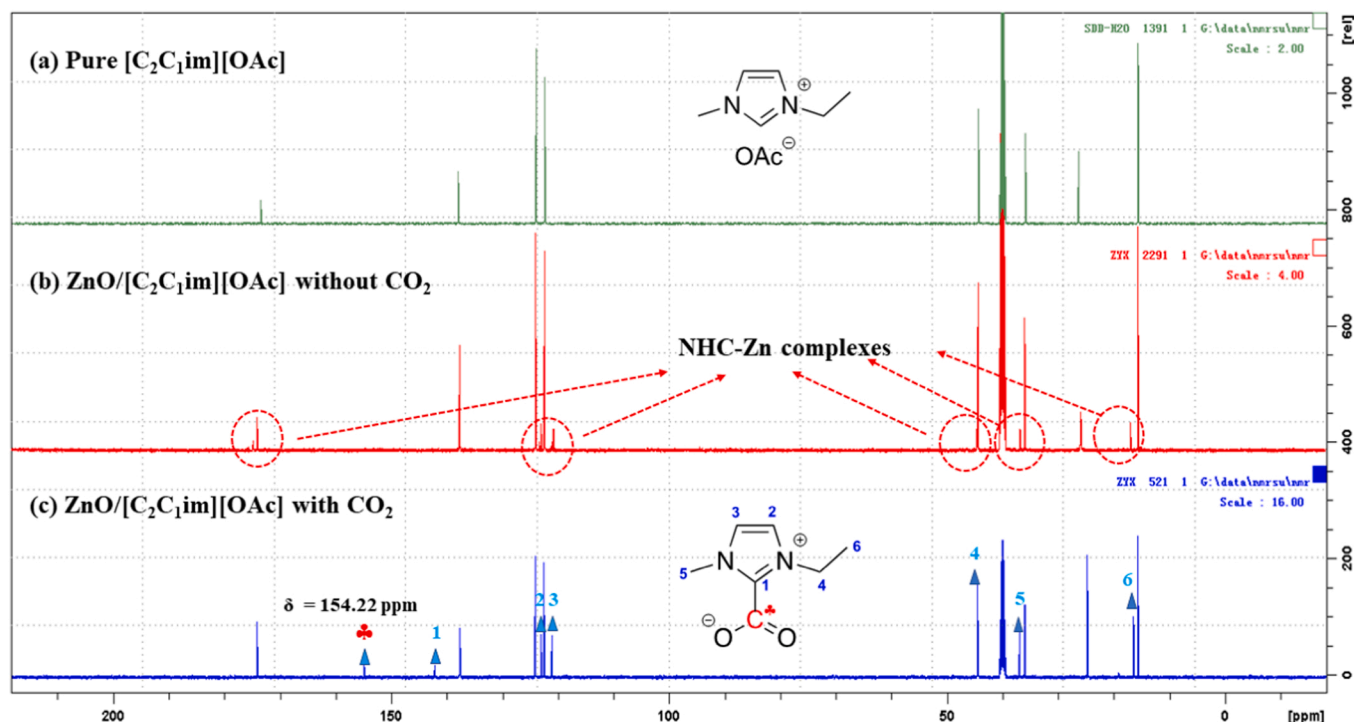


Fig. 2. ¹³C NMR analysis of pure [C₂C₁im][OAc] (a), ZnO/[C₂C₁im][OAc] without CO₂ (b), ZnO/[C₂C₁im][OAc] with CO₂ (c).

As a typical amphoteric metal oxide, ZnO could be easily dissolved by adding inorganic strong acids or bases such as HCl or NaOH. However, these direct dissolutions generally occur in aqueous solutions with drastic changes of pH. While for the synthesis of fine chemicals especially those involved with sensitive intermediates or organometallic compounds, the existence of either H₂O or the strong acid/base was strictly forbidden. Therefore, the main problem is how to dissolve ZnO into organic phases under mild conditions. Unfortunately, most of the traditional organic solvents show poor solubility for metal oxides. Apart from the traditional ones, ionic liquids (ILs) are a series of green and effective solvents which have been intensively studied and utilized nowadays for their unprecedented solubility towards some generally

insoluble compounds such as cellulose [21,22], kerogen [23], ore [24], etc. In spite of this, dissolution of metal oxides into ILs still remains a challenge due to the employed anions in common ILs are always not strong enough to solvate the metal oxides. Delightedly, chemists recently discovered that the carboxyl-functionalized ILs showed solubility for several metal oxides [25]. However, this direct dissolution was usually incomplete and required quite tedious time. Probably for this reason, few catalytic applications were reported using this strategy.

Recently, we unconsciously observed an interesting phenomenon. When we added ZnO into a carboxyl-functionalized IL such as 1-ethyl-3-methyl-imidazolium acetate ([C₂C₁im][OAc]) and stirred this suspension at 95 °C, only a brown turbid mixture could be obtained even after

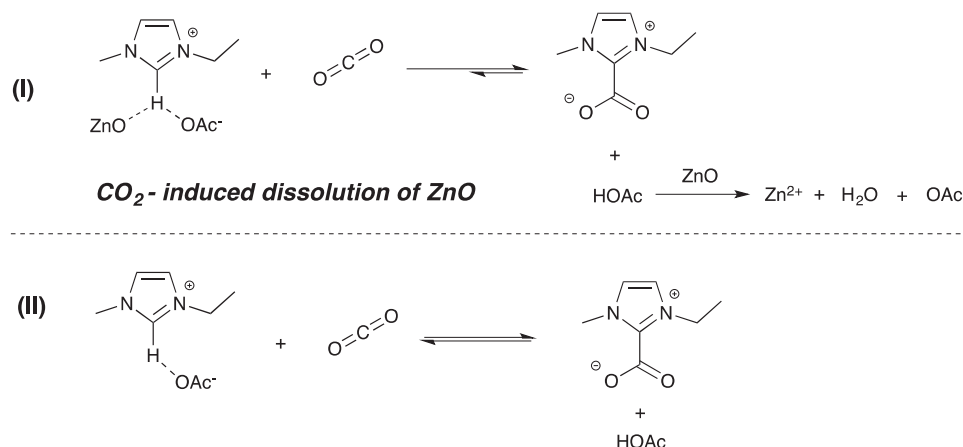


Fig. 3. The speculated pathway of the CO₂-induced dissolution of ZnO into [C₂C₁im][OAc].

days (Fig. 1, right). Nevertheless, when the seemingly irrelevant gas of CO₂ was introduced into the initial ZnO/[C₂C₁im][OAc] mixture under the same condition, this suspension would become clear transparent liquid within 10 min (Fig. 1, left), indicating the unexpected fast and complete dissolution of ZnO.

In the above experiments, the direct dissolution of ZnO into [C₂C₁im][OAc] was quite a difficult and tedious process. While in the case that CO₂ existed, ZnO would dissolve within several minutes, indicating these two processes followed totally different mechanisms. Further ¹³C NMR analysis on these two dissolved mixtures confirmed this speculation (Fig. 2). Comparing with pure [C₂C₁im][OAc] (Fig. 2a), the brown turbid mixture of ZnO/[C₂C₁im][OAc] without CO₂ showed a series of small peaks around the original imidazole signals (Fig. 2b). These peaks were found to be in accordance with the ones of the corresponding N-heterocyclic carbene zinc (NHC-Zn) complexes, which were probably generated due to the direct interaction between ZnO and [C₂C₁im] cations [25]. Conversely, these NHC-Zn complexes were not observed if ZnO was dissolved with the assistance of CO₂. Instead, a new series of strong signals appeared along with the corresponding imidazole carbons, especially a characteristic peak at $\delta = 154.22$ ppm (Fig. 2c). These peaks were finally identified to match with the ¹³C NMR resonance derived from the N-heterocyclic carbene CO₂ (NHC-CO₂) adduct [26]. Consequently, the formation of the NHC-CO₂ adduct might be the key factor that assists in the dissolution of ZnO.

Based on the above explorations, a probable pathway for the CO₂-induced ZnO dissolution in [C₂C₁im][OAc] could be speculated (Fig. 3 I). Firstly, the basic ZnO and acetate anions in [C₂C₁im][OAc] help CO₂ interact with the imidazole protons, generating NHC-CO₂ adducts and HOAc. Subsequently, the released HOAc reacts with ZnO to generate Zn²⁺ and H₂O. According to this speculated pathway, dissolution of 1

equiv. of ZnO by this CO₂-assisted way would be theoretically accompanied by the generation of 1 equiv. of H₂O. Therefore, this process could be verified by quantitative analysis of the generated H₂O by Karl Fischer titration: In an experiment for dissolving 1.6 mmol ZnO into 13.17 mmol [C₂C₁im][OAc], the water content in the employed [C₂C₁im][OAc] and the obtained dissolved mixture were measured as 0.149% and 1.331%, respectively (Table S1, supporting information). Subsequently, the theoretical value of water content after dissolution was calculated as 1.267%, which was consistent with the practical measured value (1.331%) derived from Karl Fischer titration (Part 1, supporting information). More explorations for the effect of H₂O on the ZnO/[C₂C₁im][OAc] system are supplied in Part 5 of the supporting information (Figs. S2–S7).

Having investigated the proposed dissolution pathway of ZnO, we then turned our attentions to the accompanied products of this process, namely the NHC-CO₂ adducts. In general, NHC-CO₂ adducts were considered as an activated mode of inert CO₂ [27], which had been widely utilized in numerous cases related to CO₂ conversion [28–31]. In principle, the interaction between [C₂C₁im][OAc] and CO₂ without ZnO would also generate NHC-CO₂ adducts (Fig. 3 II) [26,32,33]. However, when we mixed [C₂C₁im][OAc] with 1 bar of CO₂ at 95 °C for 10 min, only around 2% of [C₂C₁im] cations were converted into NHC-CO₂ adducts. In contrast, more than 20% of these adducts could be smoothly obtained in the presence of ZnO within the same period of time (quantification method was supplied in Figs. S8–S10, Part 6, supporting information). This was probably because ZnO would irreversibly consume HOAc, thus accelerating and shifting the equilibrium towards the NHC-CO₂ adduct side (Fig. 3 I). Therefore, the triple interaction of ILs, CO₂ and ZnO resulted in an unexpected way to rapidly produce NHC-CO₂ adducts.

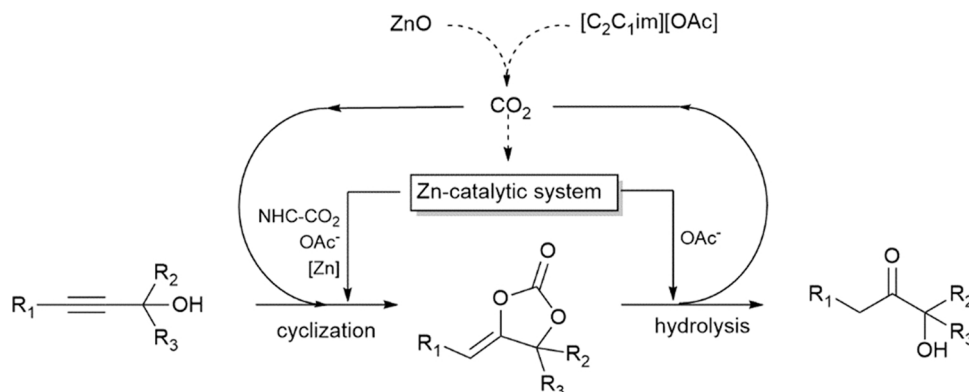


Fig. 4. CO₂-induced ZnO dissolution (dashed line) for the catalysis of CO₂-promoted hydration of propargylic alcohols (solid line).

Table 1
Screening of Zn sources and ILs.^a

| Entry | Zn source | IL | Yield ^b |
|-----------------|----------------------|--|--------------------|
| 1 | / | / | 0% |
| 2 | ZnO | / | 0% |
| 3 | / | [C ₂ C ₁ im][OAc] | 16% |
| 4 | ZnO | [C ₂ C ₁ im][OAc] | 90% |
| 5 | Nano-ZnO | [C ₂ C ₁ im][OAc] | 90% |
| 6 | Zn(OAc) ₂ | [C ₂ C ₁ im][OAc] | 72% |
| 7 | ZnMoO ₄ | [C ₂ C ₁ im][OAc] | 77% |
| 8 | ZnWO ₄ | [C ₂ C ₁ im][OAc] | 87% |
| 9 | ZnCl ₂ | [C ₂ C ₁ im][OAc] | 46% |
| 10 | ZnBr ₂ | [C ₂ C ₁ im][OAc] | 55% |
| 11 | ZnI ₂ | [C ₂ C ₁ im][OAc] | 57% |
| 12 | ZnO | [C ₄ C ₁ im][OAc] | 89% |
| 13 | ZnO | [C ₂ C ₁ im][Et ₂ PO ₄] | 48% |
| 14 ^c | ZnO | [C ₂ C ₁ im]X | 0% |

^a Conditions: 1a: (2 mmol), [Zn]: (0.4 mmol, 20 mol% based on 1a), IL: (1.6 equiv.), H₂O: (1 equiv.), 95 °C, 1 bar of CO₂, 18 h.

^b Yields were calculated by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard.

^c X = NTf₂⁻, I⁻, PF₆⁻, OTf⁻, ClO₄⁻ and HSO₄⁻.

Consequently, this CO₂-induced ZnO dissolution strategy not only established a green and effective method to convert ZnO into homogeneous state, but also provided a convenient and facile way to activate CO₂. This inspired us to apply this strategy into a CO₂-participated Zn-catalyzed reaction.

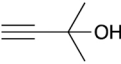
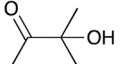
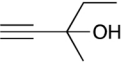
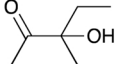
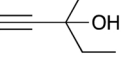
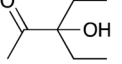
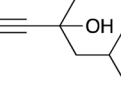
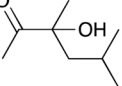
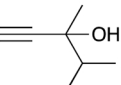
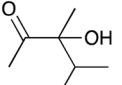
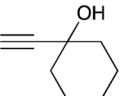
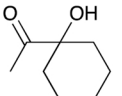
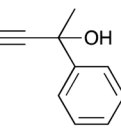
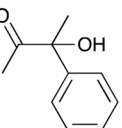
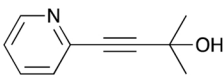
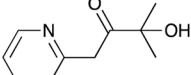
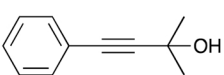
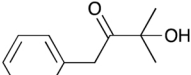
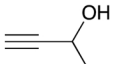
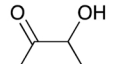
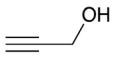
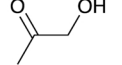
Hydration of alkynes is one of the most effective ways to construct the vital ketone skeleton [34,35]. In this area, the hydration of propargylic alcohols is significant since the corresponding products, α-hydroxyl ketones, are a series of versatile compounds that have been applied in numerous aspects such as biology, medicine, photocatalysis and synthesis [36–40]. However, the direct hydration of propargylic alcohols with H₂O always suffers from the side reactions known as Meyer-Schuster and Rupe rearrangements, which limit its practical applications to produce α-hydroxyl ketones [41,42]. Delightedly, a CO₂-promoted method for this hydration recently emerged, in which the propargylic alcohols and CO₂ are firstly cyclized to give the intermediate α-alkylidene cyclic carbonates, and the carbonates are then hydrolyzed *in situ* to deliver the desired α-hydroxyl ketones (Fig. 4, solid line) [43]. This CO₂-promoted way doesn't involve the abovementioned side reactions, thus has attracted more and more attentions nowadays. However, the reported catalytic systems for this method by far are generally limited to the rare and sensitive Ag [44] or Cu [45] ones. Moreover, high CO₂ pressure, strong organic bases or additional ligands/additives are inevitably required in most catalytic cases [46,47]. Therefore, developing greener, milder and more economical catalytic systems for this

promising hydration process is still highly desirable.

Nowadays, ILs have been considered as a series of the most promising materials for CO₂ capture and utilization due to their merits such as excellent affinity and selectivity with CO₂. Moreover, their structure tunability facilitates versatile design and modification specifically for activating CO₂, enabling ILs to be excellent catalysts for the CO₂ conversion [48–52]. On the other hand, zinc catalysis has also emerged as a new methodology to transform CO₂ owing to its green, abundant and nontoxic properties [53]. In 2016, Han et al. reported the first Zn-catalyzed example to convert CO₂ and propargylic alcohols into α-alkylidene cyclic carbonates [54], which was the first key step for the abovementioned hydration process. Very recently, Islam et al. reported a 3D-covalent organic frameworks-based zinc(II) catalyst for the same transformation [55]. The desired carbonates could be smoothly obtained under solvent-free conditions. These examples prompted us to combine ILs with Zn catalysis as a promising way to efficiently realize the CO₂-promoted hydration of propargylic alcohols.

With the above considerations in mind, we herein applied the newly discovered ZnO dissolution strategy for this CO₂-promoted transformation, in which ZnO and [C₂C₁im][OAc] interacted under CO₂ atmosphere, generating the Zn-catalytic system *in situ* (Fig. 4, dashed line) and participating in the CO₂-promoted hydration of propargylic alcohols (Fig. 4, solid line). Conveniently, this dissolution proceeded smoothly in [C₂C₁im][OAc] in spite of the existence of propargylic alcohols and H₂O. As the catalytic system, the dissolution product could *in situ* convert

Table 2Substrate scope of the ZnO/[C₂C₁im][OAc] system.

| $ \begin{array}{c} \text{R}_1-\text{C}\equiv\text{C}-\text{C}(\text{R}_2)(\text{R}_3)\text{OH} \\ \mathbf{1} \end{array} + \text{H}_2\text{O} \xrightarrow[1 \text{ bar of CO}_2]{\text{ZnO}/[\text{C}_2\text{C}_1\text{im}][\text{OAc}], 95^\circ\text{C}} \begin{array}{c} \text{R}_1-\text{CH}_2-\text{C}(=\text{O})-\text{C}(\text{R}_2)(\text{R}_3)\text{OH} \\ \mathbf{2} \end{array} $ | | | | | |
|---|---|-----------|---|------|--------------------|
| Substrate | | Product | | Time | Yield ^b |
| 1a |  | 2a |  | 24 h | 92% |
| 1b |  | 2b |  | 24 h | 89% |
| 1c |  | 2c |  | 24 h | 78% |
| 1d |  | 2d |  | 36 h | 85% |
| 1e |  | 2e |  | 36 h | 61% |
| 1f |  | 2f |  | 36 h | 89% |
| 1g |  | 2g |  | 36 h | 33% |
| 1h |  | 2h |  | 36 h | 74% |
| 1i |  | 2i |  | 36 h | 47% |
| 1j |  | 2j |  | 18 h | 43% |
| 1k |  | 2k |  | 18 h | 0% |

^a Conditions: **1**: (2 mmol), ZnO: (0.4 mmol, 20 mol% based on **1**), [C₂C₁im][OAc]: (1.6 equiv.), H₂O: (1 equiv.), 95 °C, 1 bar of CO₂.^b Yields were calculated by ¹H NMR with the 1,3,5-trimethoxybenzene as the internal standard.

propargylic alcohols into α -hydroxyl ketones in excellent yields. Notably, this Zn-catalytic system worked under atmospheric pressure with broad substrate scope and unprecedented recyclability. Significantly, the ZnO and CO₂ sources in this system could be waste pigments and flue gas respectively.

2. Experimental section

2.1. Materials and methods

Unless otherwise noted, all the compounds including the substrates, zinc salts, ionic liquids, and solvents were commercially purchased from Aladdin, Sigma-Aldrich, TCI, Macklin, Alfa in China and used directly without further purification and dryness. The CO₂ (99.9%) and mimetic flue gas (80 vol% N₂, 20 vol% CO₂) used for purging and reacting were supplied by Wuhan Zhongchunhua Science and Technology Ltd. The pigment of zinc white was purchased from kusakabe (code: WA274). The pigment of titanium zinc white was supplied by Rubens (code: 102). With regard to the related analysis and characterization, NMR spectra were recorded on a Bruker AVANCE III HD 500 MHz spectrometer at ambient temperature, operating at 500 MHz for ¹H and at 126 MHz for ¹³C. Peak frequencies were referenced *versus* an internal standard (TMS), with the chemical shifts at 0 ppm for ¹H NMR and against the solvent (CDCl₃, 77.00 ppm; DMSO-*d*₆, 39.90 ppm) for ¹³C NMR, respectively. X-Ray Fluorescence (XRF) was taken on a Panalytical Axios Fluorescence Spectrometer. Water content was analyzed by a Mettler-Toledo V20S moisture meter.

2.2. General procedures for the CO₂-promoted hydration of propargylic alcohols

Pure ZnO (0.4 mmol, 20 mol%) or dry pigment (contained 0.4 mmol ZnO), [C₂C₁im][OAc] (3.2 mmol, 1.6 equiv.), propargylic alcohol (2 mmol), H₂O (2 mmol) were added to a 15 mL Schlenk tube. The system was quickly purged 3 times with CO₂ or flue gas. Then the mixture was stirred at 95 °C under atmospheric pressure for the required time. Upon completion, the mixture was extracted with diethyl ether (15 mL \times 3). The upper layers were combined. Then the solvent was removed under reduced pressure to obtain the crude product, which was further purified by column chromatography (petroleum ether/ethyl acetate 100:1–20:1 v/v) on silica gel.

2.3. General procedures for the investigations on the recyclability

When the abovementioned reaction was completed, the mixture was extracted with diethyl ether (15 mL \times 3). The lower layer was dried under vacuum at 80 °C for 4 h to totally remove the volatile residuals in the system. Subsequently, this catalytic system was directly used for the next round.

3. Investigations on the catalytic performance

3.1. Optimization of the catalytic components

In order to demonstrate the superiority of the catalytic system generated from the CO₂-induced dissolution of ZnO in [C₂C₁im][OAc], we compared the catalytic activity of different systems composed of various Zn sources and imidazole-based ILs. The CO₂-promoted hydration of 2-methyl-3-buten-2-ol (1a) was explored as a model reaction and the catalytic results were listed in Table 1. Initially, the blank experiment indicated that this hydration would not occur without catalysis (entry 1). Moreover, addition of individual ZnO couldn't promote this reaction (entry 2). On the other hand, the [C₂C₁im][OAc] IL behaved slight activity with a poor yield of 16% (entry 3). In contrast, when both of ZnO and [C₂C₁im][OAc] were introduced, the reaction proceeded smoothly to provide desired product 2a in an excellent yield (entry 4).

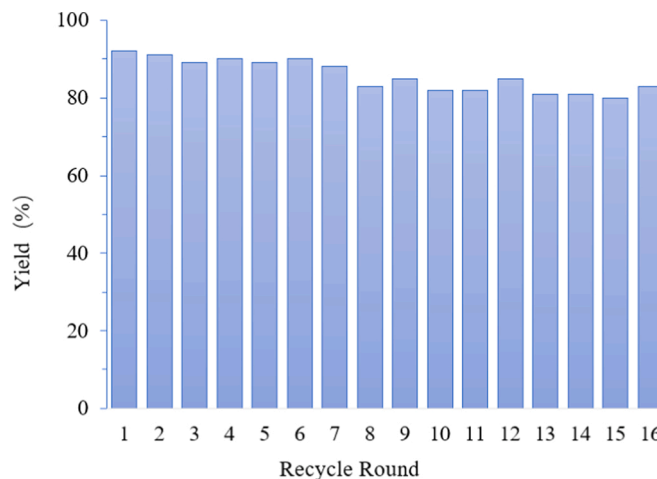


Fig. 5. Investigation on the recyclability of the ZnO/[C₂C₁im][OAc] system.

Subsequently, different zinc sources including ZnO, Zn(OAc)₂, ZnMoO₄, ZnWO₄, ZnCl₂, ZnBr₂, ZnI₂ were screened in the presence of [C₂C₁im][OAc] (entries 4–11). Delightedly, most of them gave moderate to high yields for α -hydroxy ketones (2a). Furthermore, it should be noted that the catalytic activity of these zinc sources was related to their anions. When basic OAc[−], WO₄^{2−} and MoO₄^{2−} were employed, the desired product could be produced with high yields (entries 6–8). While for Cl[−], Br[−], or I[−], product 2a was obtained in merely moderate yields (entries 9–11). Specifically, ZnO exhibited the best catalytic performance among all the zinc catalysts. Moreover, the same yields were obtained by the normal ZnO and nano-ZnO (entries 4 vs. 5). Afterwards, various ILs were introduced for the model reaction to investigate their catalytic activity (entries 12–14). It could be observed that the ILs with anions of OAc[−] exhibited the best catalytic activity (entries 4, 12). Replacing its ethyl imidazole cation with an *n*-butyl one would not affect its excellent activity (entry 4 vs. 12). In the cases of other anions, Et₂PO₄[−] exhibited moderate activity for the model reaction (entry 13), while NTf₂[−], I[−], PF₆[−], OTf[−], ClO₄[−] and HSO₄[−] didn't give satisfactory results (entry 14). Consequently, the CO₂-induced ZnO dissolution in the specific IL of [C₂C₁im][OAc] would generate a highly efficient catalytic system (named as ZnO/[C₂C₁im][OAc] system in the following paragraphs), which performed superior activity over the other investigated systems herein.

3.2. Exploration for the substrate scope

In the abovementioned investigations, an efficient ZnO/[C₂C₁im][OAc] catalytic system was established based on the CO₂-induced ZnO dissolution strategy. After further optimizing its catalytic conditions (Table S2, Part 2, supporting information), we started to explore the substrate scope of this system through the hydration of different terminal or internal propargylic alcohols, with the incorporation of various alkyl, cycloalkyl or aryl groups (Table 2). To our delight, these propargylic alcohols didn't show obvious influence on the ZnO dissolution process and the corresponding α -hydroxy ketone products (2a–j) were successfully obtained in moderate to excellent yields. In detail, tertiary propargylic alcohols with less sterically hindered methyl or ethyl groups were easier to give high yields than those with larger phenyl or pyridyl groups (1a–c vs. 1g–i), indicating that the steric profile of the substituents had visible effects on the formation of the corresponding α -hydroxy ketones. Moreover, the terminal tertiary propargylic alcohols generally behaved higher reactivity than the internal ones for the target reaction. In addition to the tertiary ones, a secondary propargylic alcohol (1j) and a primary propargylic alcohol (1k) were also tested. In these experiments, 1j gave a relatively low yield of 43%, while 1k didn't show reactivity for this CO₂-promoted hydration. This might be

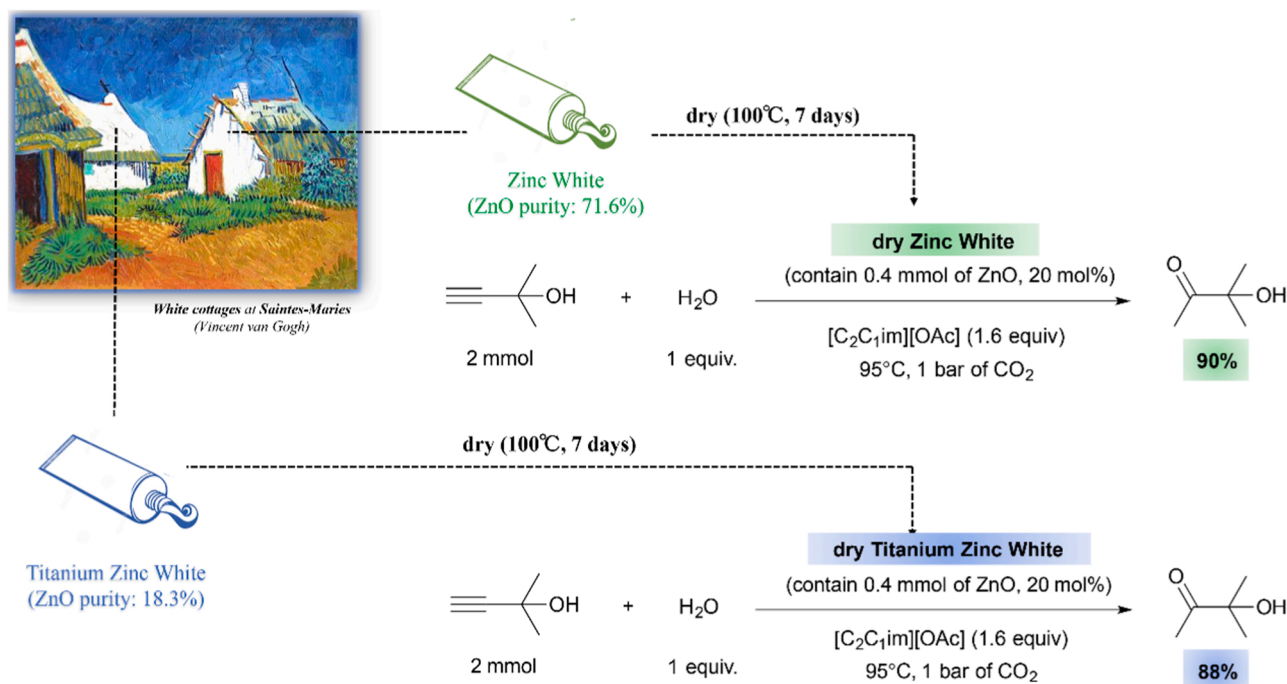


Fig. 6. CO_2 -promoted hydration of 1a catalyzed by ZnO-containing white pigments.

attributed to the lack of *gem*-dialkyl effect in these primary and secondary substrates, which limited their cyclization with CO_2 to give the key intermediate α -alkylidene cyclic carbonates [55–57].

3.3. Recyclability

In addition to the catalytic activity as well as the substrate scope, the recyclability and reusability were also pivotal properties for comprehensively evaluating a catalytic system. In this aspect, the recycling performance of the $\text{ZnO}/[\text{C}_2\text{C}_1\text{im}][\text{OAc}]$ system was investigated using 1a as the model substrate. Benefited from the stability of the IL and zinc

components, this catalytic system showed unprecedented performance in this evaluation, which could be recycled and reused at least 16 times with steady yields higher than 80% (Fig. 5). To the best of our knowledge, this is the maximum round number ever reached for the CO_2 -promoted hydration reaction. These results indicated the excellent recyclability and reusability of the $\text{ZnO}/[\text{C}_2\text{C}_1\text{im}][\text{OAc}]$ system.

3.4. Waste pigments as the ZnO source

In all the previous reports for the CO_2 -promoted hydration reaction, the vital metal catalysts were directly purchased from commercial

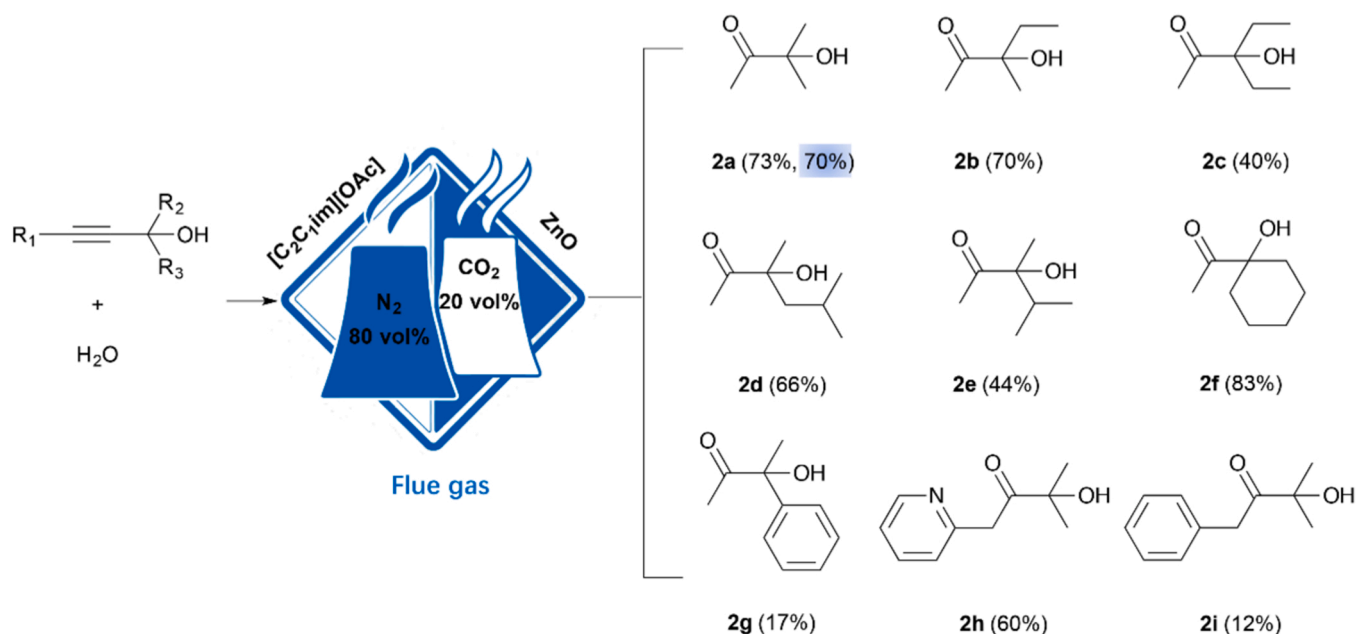
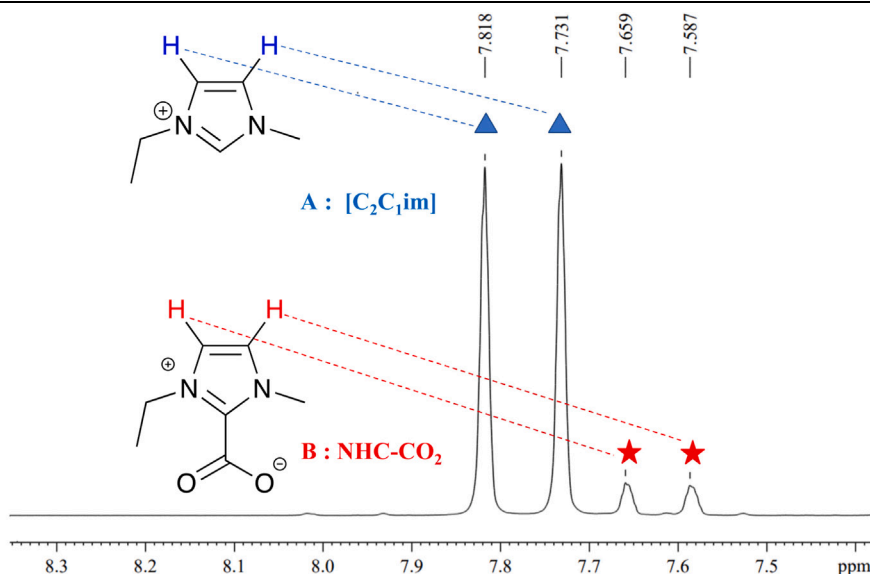


Fig. 7. Investigations on the catalytic activity under the flue gas atmosphere. (Note: Reaction conditions, time and yields calculation were the same with Table 2 except that the pure CO_2 was replaced by the flue gas. The yield (70%) marked with blue color was obtained when pure ZnO was replaced by the titanium zinc white.)

Table 3Relationship between catalytic yields and NHC-CO₂ amounts for different Zn sources.

| Entry | Zn salt | Yield (%) | A : B | B/(A+B) (%) |
|-------|----------------------|-----------|-------|-------------|
| 1 | ZnO | 90 | 6:1 | 14.3 |
| 2 | Nano ZnO | 90 | 6:1 | 14.3 |
| 3 | ZnWO ₄ | 87 | 11:1 | 8.3 |
| 4 | ZnMoO ₄ | 77 | 21:1 | 4.5 |
| 5 | Zn(OAc) ₂ | 72 | 22:1 | 4.3 |
| 6 | ZnCl ₂ | 46 | 25:1 | 3.8 |
| 7 | ZnBr ₂ | 55 | 30:1 | 3.2 |
| 8 | ZnI ₂ | 57 | 35:1 | 2.8 |

* **A** = [C₂C₁im], **B** = NHC-CO₂

companies with high purity. This might be beneficial for avoiding the interference of impurities and obtaining more exact catalytic data. However, this also limited the studies and applications of these catalysts only in the stage of laboratories up to now. Therefore, after employing pure ZnO for the above investigations on the catalytic performance, we then paid our attentions to other more general ZnO-containing products. Nowadays, ZnO has been generally applied in numerous areas of our daily life. One well-known example is its utilization in art area, especially in painting for the well-known white pigment “zinc white”, which is the most transparent white color recommended for glazing, scumbling

and alla prima painting. Apart from zinc white, another excellent mixing pigment, namely “titanium zinc white” consisted of ZnO and TiO₂, is the most useful all-purpose oil painting white that combines the soft texture and opacity of titanium with the creamy transparency of zinc. As two representative ZnO sources, zinc white and titanium zinc white were selected for our attempts to replace high-purity ZnO in the catalysis of CO₂-promoted hydration. According to the recipe, these pigment products generally consisted of ZnO, other inorganic Ti, Ba, Ca, Al compounds and organic additives such as adhesive glues, oils *etc.* Therefore, the ZnO content in these pigment samples were first analyzed by XRF.

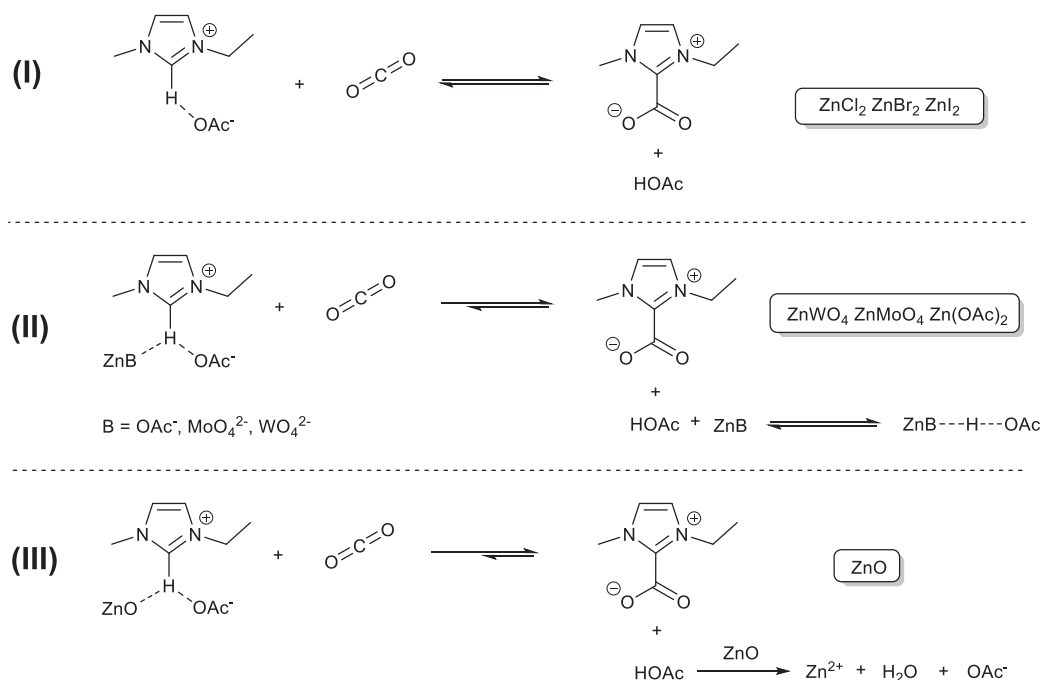


Fig. 8. Interaction processes of [C₂C₁im][OAc] and CO₂ in the situations of different Zn sources.

The result indicated that the zinc white contains 71.8% of ZnO and titanium zinc white contains only 18.3% of ZnO. Subsequently, these two samples were put in the oven (100 °C, 7 days) to simulate its drying and expiring process. Once completed, these waste pigments were directly employed as the ZnO sources without further purification for the catalysis of the CO₂-promoted hydration of 1a under its optimal conditions. After the required time, two comparable yields of 90% and 88% were successively obtained (Fig. 6). These results indicated the high tolerance and practicability of the ZnO/[C₂C₁im][OAc] system, which provided a potential method for treatment and reutilization of ZnO waste (e. g. expired pigments, metal slags, exhausted batteries, etc.).

3.5. Flue gas as the CO₂ source

In the above explorations, the ZnO/[C₂C₁im][OAc] system exhibited excellent tolerance and compatibility for impure ZnO such as waste pigments, which largely facilitated its potential in practical application. Following this idea, we then considered that the high purity CO₂ employed in this CO₂-promoted hydration process might also be replaced by impure CO₂ sources, such as the flue gas from the combustion of fossil fuels. Generally, the major components of the dry flue gas are N₂ and CO₂ with the ratio between 9:1–7:3 approximately. Therefore, mimetic flue gas composed of N₂ (80 vol%) and CO₂ (20 vol %) was selected as a model to explore its activity for the target hydration. All the substrates 1a–i were screened again under 1 bar of flue gas catalyzed by the ZnO/[C₂C₁im][OAc] system (Fig. 7). Compared these cases with the ones in pure CO₂, most of the substrates could be smoothly obtained under the same conditions, albeit the yields of the products slightly decreased for around 6–19%. These results revealed the effective promotion of the flue gas for the target reactions. Finally, the titanium zinc white was also tried together with the flue gas (Fig. 7, 2a, blue color marked), which indicated that the simultaneous employments of impure ZnO and CO₂ would not affect the excellent activity of the ZnO/[C₂C₁im][OAc] system.

4. Mechanistic investigation

4.1. Exploration for the NHC-CO₂ adducts

In the above investigations, the superior catalytic performance of the ZnO/[C₂C₁im][OAc] system were detailedly identified. Subsequently, we further explored why ZnO behaved much better than the other Zn salts. In our previous investigations on the CO₂-induced ZnO dissolution, we confirmed that a considerable amount of NHC-CO₂ adducts would be simultaneously generated during this process. Therefore, these adducts might be a key factor that affected the catalytic activity.

In order to explore whether these NHC-CO₂ adducts were beneficial for the target reaction, we firstly investigated the amounts of the generated NHC-CO₂ adducts in different reaction mixtures respectively catalyzed by ZnO, nano-ZnO, ZnWO₄, ZnMoO₄, Zn(OAc)₂, ZnCl₂, ZnBr₂, ZnI₂ combined with [C₂C₁im][OAc] (following the conditions in Table 1). These reaction mixtures were sampled and directly analyzed by ¹H NMR. In the obtained spectra (Table 3), the peaks at $\delta = 7.818$, 7.731 represented two characteristic protons of [C₂C₁im], meanwhile, the peaks at $\delta = 7.659$, 7.587 represented the same two protons in NHC-CO₂ adducts [33,58]. Based on this, the ratio of generated NHC-CO₂ (B) vs. remaining [C₂C₁im] (A) could be calculated by integration (Fig. S1, Part 3 of supporting information), and the results were listed in Table 3. In the process that ZnO participated, 14.3% of [C₂C₁im] was converted into the NHC-CO₂ adducts, while this value was only 4.3–8.3% for ZnWO₄, Zn(OAc)₂, ZnMoO₄ and 2.8–3.8% for ZnCl₂, ZnBr₂, ZnI₂. More importantly, it could be clearly observed that the trend of NHC-CO₂ amounts matched with that of the yields in Table 3. In another word, the more NHC-CO₂ adducts generated, the higher yield obtained. These results confirmed that NHC-CO₂ adducts were beneficial for the reaction. Therefore, the superior catalytic performance of the ZnO might be attributed to its strongest ability to generate NHC-CO₂ adducts in the dissolution process.

In fact, the different ability to generate NHC-CO₂ adducts of various Zn sources could be explained by the chemical equilibrium between [C₂C₁im][OAc]/CO₂ and NHC-CO₂/HOAc (Fig. 8). For the Zn salts such as ZnCl₂, ZnBr₂, ZnI₂, their anions would not affect the generation of NHC-CO₂ (Fig. 8 I). While in the cases of ZnWO₄, Zn(OAc)₂, ZnMoO₄,

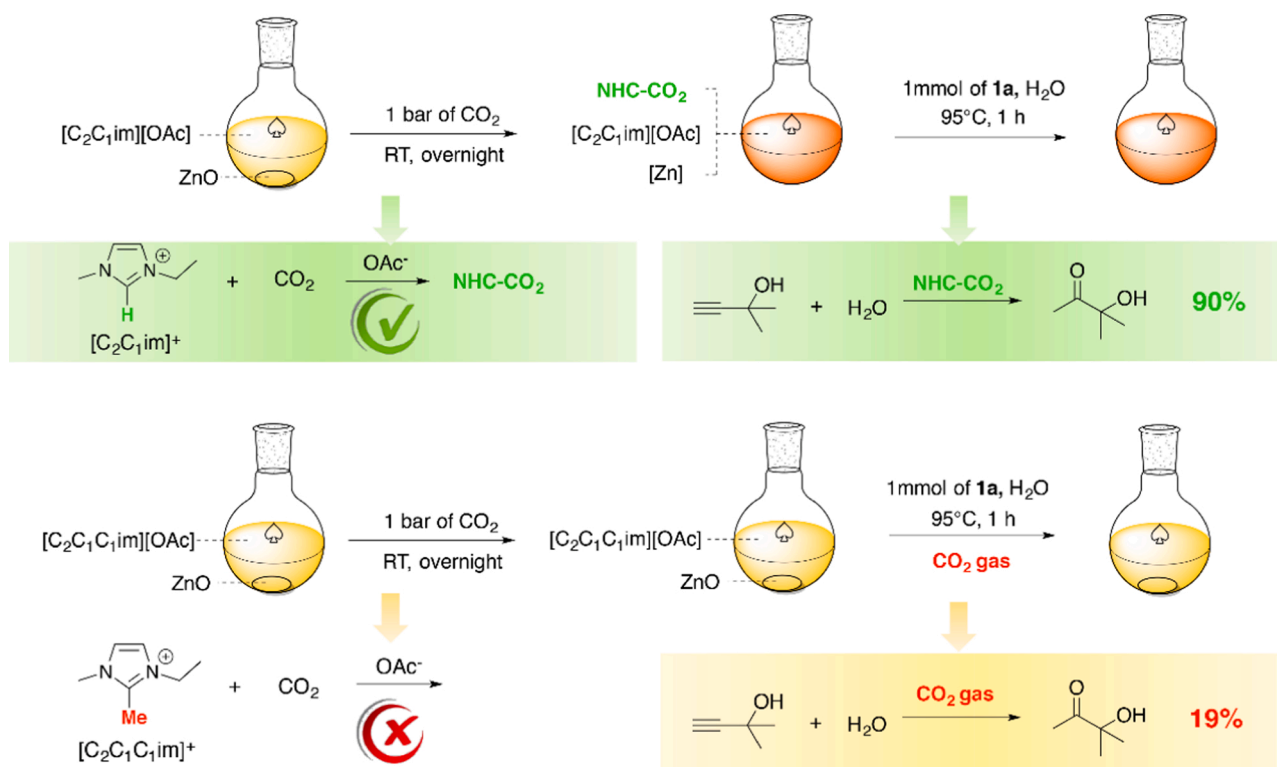
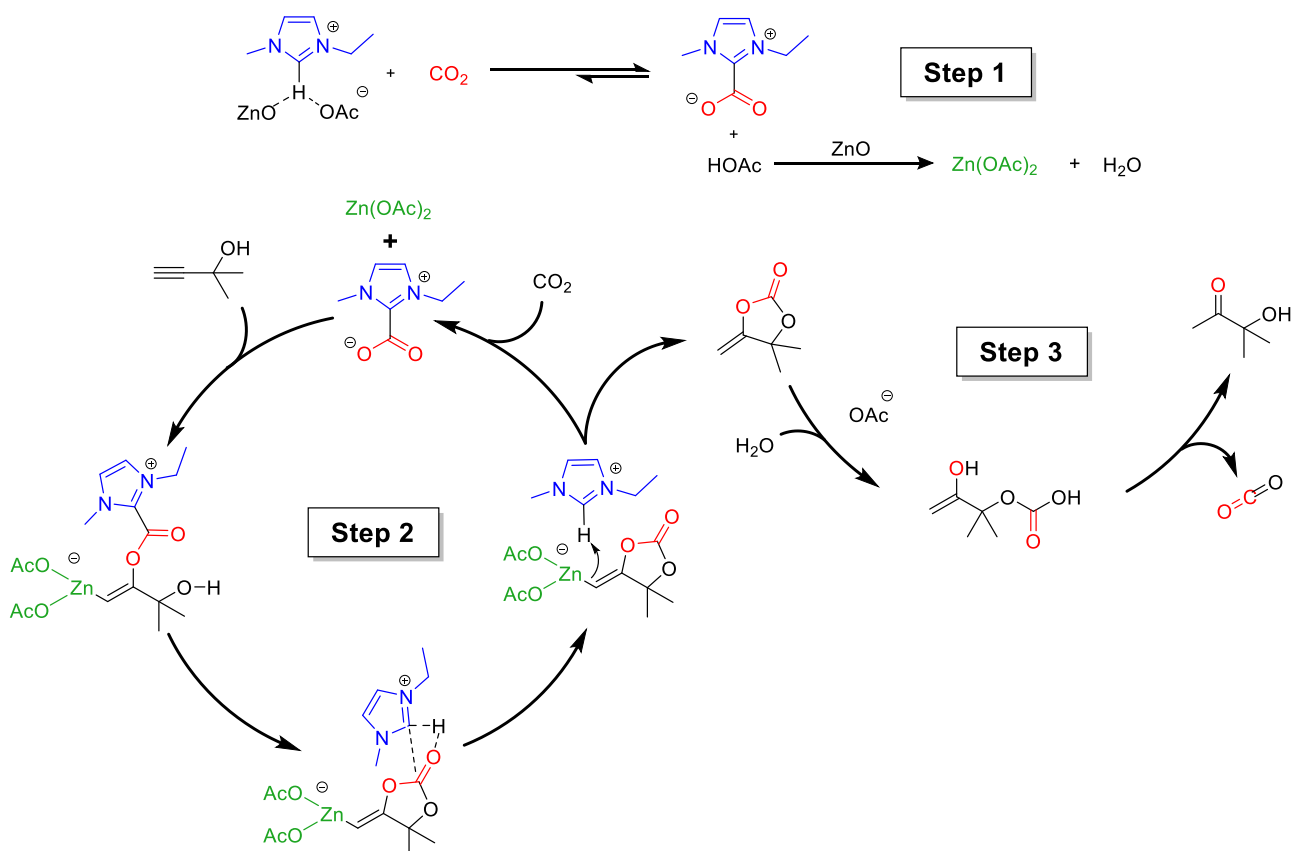


Fig. 9. Paralleled experiments for evaluating the reactivity of NHC-CO₂ and CO₂.



Scheme 1. A possible catalytic mechanism of NHC-CO₂ for the CO₂-promoted hydration of propargylic alcohols.

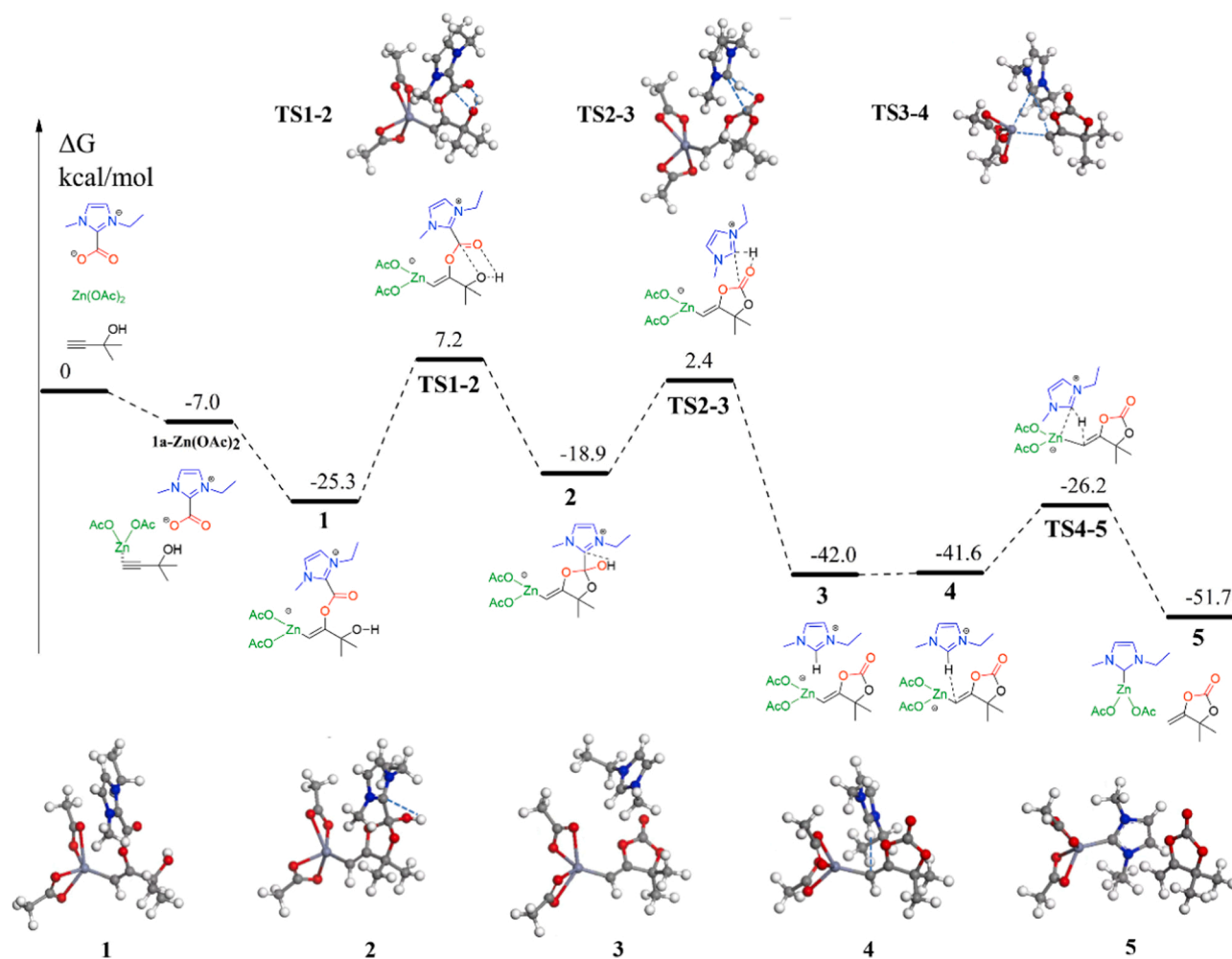


Fig. 10. The energy profile and the schematic structures of all the transition states and intermediates involved in the reaction pathway catalyzed by NHC-CO₂ adduct.

the basic anions might combine with the HOAc in the abovementioned equilibrium, shifting it towards the NHC-CO₂/HOAc side (Fig. 8 II). However, this combination was also an equilibrium process, thus the fixation of HOAc was not permanent. On the contrary, the HOAc could be irreversibly converted into H₂O and OAc⁻ when ZnO was employed as the catalyst, thus the equilibrium would be largely shifted toward the direction of NHC-CO₂ adducts (Fig. 8 III). Therefore, ZnO would produce the most amount of NHC-CO₂ adducts, while ZnWO₄, Zn(OAc)₂, ZnMoO₄ exhibited moderate ability and ZnCl₂, ZnBr₂, ZnI₂ gave relatively poor yields.

Based on the experimental data, we confirmed that more NHC-CO₂ adducts would promote the target reaction in a better fashion. This inspired us that the reactivity of NHC-CO₂ adducts might be stronger than the normal CO₂ molecules in the target reaction. In order to directly compare their reactivity, a similar IL of 1-ethyl-2,3-dimethyl-imidazolium acetate ([C₂C₁C₁im][OAc]) was firstly synthesized according to the literature [59]. In this IL, the active proton in the imidazole cation was replaced by an inert methyl group, which would block the generation of the NHC-CO₂ adduct. Subsequently, two paralleled experiments were performed as below (Fig. 9): 5 mmol of [C₂C₁im][OAc] and [C₂C₁C₁im][OAc] were respectively added with 1 mmol of ZnO. These two systems were stirred under 1 bar of CO₂ overnight at room temperature. During this period, the [C₂C₁im][OAc]/ZnO system would generate NHC-CO₂ adducts and dissolve ZnO, while the [C₂C₁C₁im][OAc]/ZnO system couldn't undergo this process. Once finished, 1 mmol of 1a and H₂O were added into the [C₂C₁im][OAc]/ZnO system

for further reaction without gaseous CO₂. In this reaction, NHC-CO₂ was the only CO₂ source. On the other hand, the [C₂C₁C₁im][OAc]/ZnO system was also added with 1 mmol of 1a and H₂O while the system was left under 1 bar of CO₂ for the hydration reaction. Since the NHC-CO₂ adducts couldn't be generated in this system, the gaseous CO₂ would be the only CO₂ source. After 1 h, these two reactions were stopped and their yields were directly calculated. The results showed that the [C₂C₁im][OAc]/ZnO system gave almost stoichiometric conversion, while the [C₂C₁C₁im][OAc]/ZnO system gave only 19% yield. These results indicated that the NHC-CO₂ adducts behaved stronger reactivity than the normal CO₂ molecules in the CO₂-promoted hydration of propargylic alcohols.

4.2. Proposed catalytic mechanism

Having identified the excellent reactivity of NHC-CO₂ adducts, we then speculated a possible catalytic mechanism for the CO₂-promoted hydration of propargylic alcohols involved with NHC-CO₂ adducts (Scheme 1). In the first step, CO₂ induced the dissolution of ZnO and the NHC-CO₂ adducts were generated simultaneously. In the second step, the negative oxygens in NHC-CO₂ adducts attacked the triple bonds in the substrates with the aid of Zn species. Once the C-O bonds were formed, the negative oxygens in OH groups would attack the positive carbon centers of NHC-CO₂ adducts to generate the five-membered ring of carbonates. Simultaneously, the hydroxyl protons would be transferred to the NHCs to generate imidazoles. Finally, these protons were

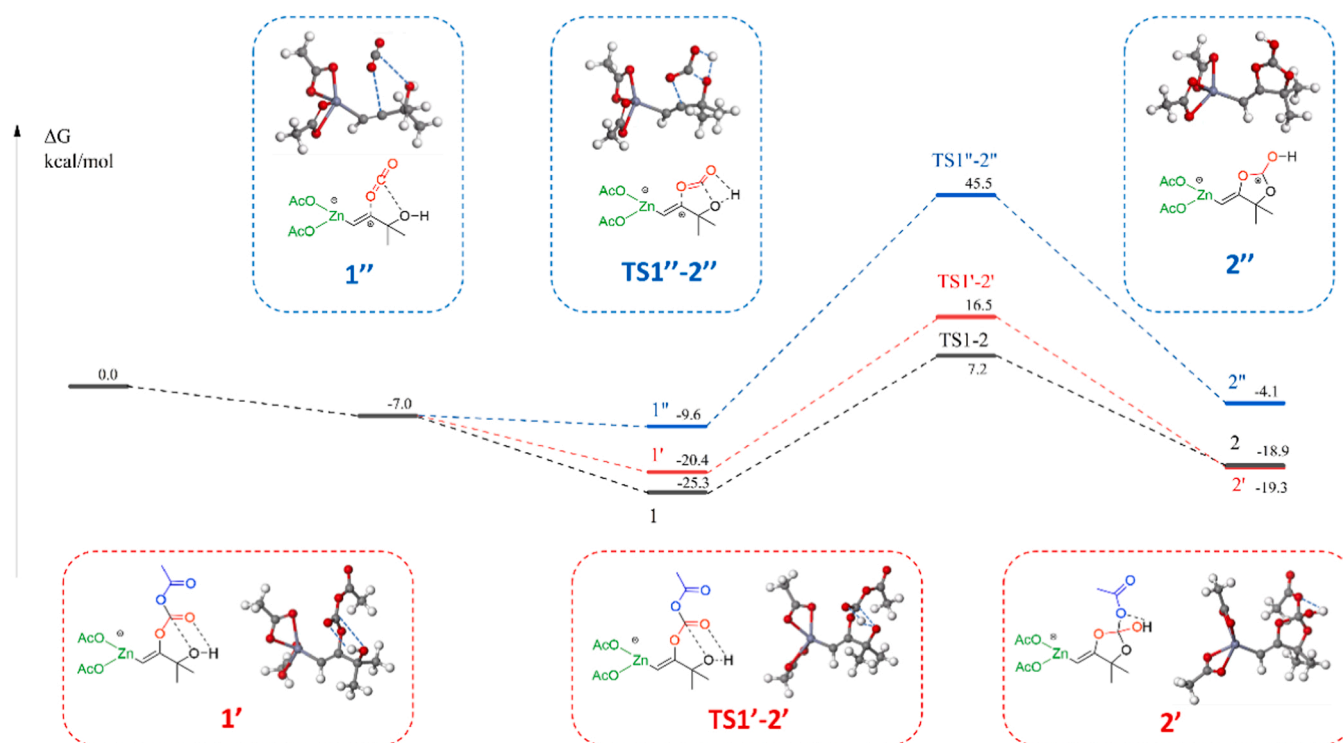


Fig. 11. The energy profile and the schematic structures of the transition state and intermediates involved in the CO₂ insertion pathway. (black: NHC-CO₂; blue: CO₂; red: OAc-CO₂).

given back to obtain the α -alkylidene cyclic carbonates, while the NHCs continued to capture CO₂ and participated in the next round. In the third step, the generated carbonates were hydrolyzed *in situ*. Subsequently, the keto-enol tautomerization occurred and the final products were generated by releasing one equivalent of CO₂.

4.3. Density functional theory (DFT) calculation

In the above mechanism, the second step was the crucial one which accomplished the assembly of CO₂ fragments and substrates. Therefore, this step was detailedly investigated by means of DFT calculation (Fig. 10). Firstly, the Zn species activated the substrates to obtain 1a-Zn (OAc)₂ complexes (−7.0 kcal/mol). Then the NHC-CO₂ adducts started to attack these complexes and attached the CO₂ segments with the triple bonds (1, −25.3 kcal/mol). Once the C-O bonds were formed, the hydroxyl oxygens attacked the carbon centers of NHC-CO₂ to give the five-membered rings (2, −18.9 kcal/mol) through the transition state (TS1-2, 7.2 kcal/mol). Then, the CO₂ segments disconnected with the NHCs and the hydroxyl proton migrated to these NHCs (TS2-3), giving the imidazoles and Zn-carbonates complexes (3, −42 kcal/mol). Eventually, the imidazoles would approach to the Zn-C bonds (4, −41.6 kcal/mol) and give the protons back to the organic skeletons to obtain the final products (5, −51.7 kcal/mol) through the transition state (TS4-5, −26.2 kcal/mol).

In the abovementioned calculation, intermediate 1 to 2 was the step that proceeded the CO₂ insertion process. Therefore, the energy barriers of this step could reveal the reactivity of different CO₂ sources. It was worth noting that apart from the NHC-CO₂ adducts, CO₂ might also be activated with the assistance of OAc[−] [60–62]. Therefore, these three possible CO₂ sources, namely CO₂, NHC-CO₂ adducts and OAc-CO₂ complexes were applied to the DFT calculation for their performance in the step of intermediate 1 to 2. Their energy profiles were illustrated in Fig. 11. Based on the calculation results, the overall free energy barrier for the electrophilic attack of CO₂ molecules and the following intramolecular cyclization was calculated to be 55.1 kcal/mol (Fig. 11, blue

line), which was too high for the reaction to occur spontaneously. With the aid of OAc[−], this energy barrier would decrease to 36.9 kcal/mol (Fig. 11, red line), while its contribution to prompt the reaction was still less than that of the NHC-CO₂ adducts. For the situations of these NHC-CO₂ adducts, the overall free energy barrier is only 32.5 kcal/mol (Fig. 11, black line), which was the lowest level among these CO₂ sources. These results indicated that the NHC-CO₂ adducts were more favorable for this catalytic process compared with CO₂ or OAc-CO₂, which was in accordance with the previous conclusion obtained by the paralleled experiments in Fig. 9.

5. Conclusion

In conclusion, an extraordinary dissolution of ZnO into the ILs induced by CO₂ was discovered. This dissolution could be accomplished in minutes, and the resultant mixture was identified to be an efficient Zn-based catalytic system for the hydration of propargylic alcohols which exhibited broad substrate scope as well as the strongest recyclability reported by far. Moreover, this system could directly employ the waste pigments as the ZnO source and exhibit excellent catalytic activity under atmospheric flue gas. Further mechanistic investigations revealed that the dissolution of ZnO was related with the chemical equilibrium between ILs, ZnO and CO₂. More importantly, this dissolution meanwhile shifted the equilibrium to produce more NHC-CO₂ adducts, which were proved to show better reactivity than CO₂ by experiments as well as DFT calculation.

CRediT authorship contribution statement

Yongxing Zhang: Investigation, Methodology, Resources, Writing – original draft. **Jia Hu:** Investigation, Formal analysis. **Yong Xu:** Investigation, Data curation, Methodology. **Xiangyu Yan:** Investigation, Data curation, Methodology. **Siqi Zhang:** Validation, Manuscript checking. **Kang Duan:** Validation, Manuscript checking. **Cheng Chen:** Project administration, Writing – review & editing. **Ye Yuan:** Supervision,

Writing – review & editing, Project administration, Manuscript final version approval, Performed the simulation (Theoretical calculation). **Francis Verpoort**: Supervision, Funding acquisition, Manuscript editing, Manuscript final version approval.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2022.121270](https://doi.org/10.1016/j.apcatb.2022.121270).

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